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CONTENTS

	PAGE
Cyclization of Hydrocarbons. By S. J. GREEN	179
Spring Tension Balance for Bouncing Pin. By P. DRAPER	209
Obituary	214
Abstracts	335A–354A
Institute Notes	i

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THE CYCLIZATION OF HYDROCARBON MIXTURES.*

By S. J. Green, B.Sc., A.I.C.

Introduction.

The conversion of non-aromatic hydrocarbons into aromatics within convenient temperature range constitutes one of the most important advances in recent hydrocarbon chemistry. The process is attractive not only for the production of high-octane fuel, but also for the production of pure aromatic hydrocarbons and for many potential uses in analytical chemistry, etc.

Considerable work has been done on the dehydrogenation-cyclization reactions of pure hydrocarbons, but little has been published on the conversion of hydrocarbon mixtures in this way. In the present work, a preliminary examination of the possibilities, there is no contribution to the theory of the mechanisms of cyclization reactions, but some interesting facts are disclosed and some potentialities of the dehydrogenation cyclization process are indicated.

By " thermal " and " catalytic " aromatization two different processes are understood. In the first the nature of the aromatic hydrocarbons produced depends on the temperature, and in the second, on the catalyst and the feed. The thermal aromatization of heptane, for example, would lead to an equilibrium mixture (theoretically) of benzene and other aromatics, while the cyclization of the same hydrocarbon would produce toluene.

Previous Work.

When the catalytic aromatization of hydrocarbon mixtures is considered, reactions other than pure dehydrogenation-cyclization must be expected to influence the conversion. For this reason aromatization in general is considered in the literature review below. There is considerable published work on the production of aromatics from other hydrocarbons, and only a selection is indicated here.

Aromatics from Unsaturateds.

In 1931, Mailhe and Renaudie [1] heated mixed amylenes up to 670° C. for several hours, and obtained aromatics in the product, together with some tar. Taylor and Turkevich [2] converted various branched and straight-chain olefines into mixtures containing aromatics using chromium sesquioxide gel at temperatures ranging from 400° to 475° C. Various olefines and paraffins were converted into aromatics by Grosse, Morrell, and Mattox [3]: octane was converted into a mixture containing aromatics at temperatures of 450–700° and contact times of 0·1–10 seconds over catalysts such as

* Paper received 24th June, 1942.

Cr, Mo, V, Ti, on activated alumina. Cyclic olefines have been converted into aromatics by various workers,[4, 5, 6] and some simple cyclic diolefines were similarly converted,[7, 8, 9] using Pd catalyst in both cases. Using Cr_2O_3 gel, Goldwasser and Taylor [10] investigated the aromatization of heptane, heptene, and hexene isomers.

The process of cyclization involves dehydrogenation, and a useful summary of the literature on catalytic dehydrogenation of hydrocarbons is given in the *Twelfth Report of the Committee on Catalysis* (New York, 1940).

Paraffins to Aromatics.

Egloff [11] reported as early as 1916 the conversion of hexane into toluene and other aromatics using a steel tube at temperatures from 450° C. to 725° C. More recently the U.O.P. workers [3, 12] have converted hexane and heptane into aromatics and unsaturateds over oxides of Cr, Mo, Ti on alumina and over Cr_2O_3 gel, the products in many cases containing more than 50 per cent. aromatics. Moldavski and co-workers [13] converted octane and heptane into aromatics using Cr_2O_3 gel and also zinc oxide.

In their rather comprehensive work these workers showed that *n*-octane passed over Cr_2O_3 gel at 400° C. produced mainly *o*-xylene and ethyl benzene together with some *m*- and *p*-xylene. Di*iso*butyl was converted into *p*-xylene, and butyl benzene converted into naphthalene under similar conditions. Conversion losses were found of the order of 50 per cent., but volumes of the order of only 20 c.c. were used. Their general conclusions were that increase in the contact time increases aromatics and decreases unsaturated hydrocarbons in the products from paraffins, while naphthenes produced are negligible. Other catalysts used for the conversion of octane included TiO_2, MoO_2 on charcoal, MoS_2, carbon on iron turnings [14] and nickel on zinc oxide.[15] For the aromatization of the decanes chromium–copper–phosphorus and chromium–molybdenum [16] have been used. In order to avoid carbon formation, which is likely to accompany dehydrogenation at the higher reaction temperatures when using nickel catalysts, it has been suggested in a recent patent [17] that the reaction should be carried out in the presence of steam in a chromium-steel tube.

Taylor and Jovis found that Cu–Mg catalysts are less active than Ni for carbon–carbon bond splitting in dehydrogenation-cyclization reactions.

Naphthenes to Aromatics.

*cyclo*Hexane has been converted into benzene over various catalysts at temperatures varying from 190° C. to 540° C. Moldavski and co-workers [14] used ZnO, TiO_2, MoO_2 on charcoal, MoS_2, active charcoal, and carbon on iron; Balandin [18] used Ni on alumina and later [19] alumina alone. Zelinsky [20] used palladium at 300° C. to obtain benzene as early as 1911, but recently he prepared toluene from *cyclo*hexane using Ni on $Al(OH)_3$, and benzene when using platinum.[21] In 1936, Ipatieff and Komarewsky [22] produced toluene, benzene, and methane from *cyclo*hexane by passing it over nickel-aluminum at 350° C. Alumina,[23] copper,[24] and copper-chromium [25] have also been used successfully. Jubhard [26] showed that Fe, Cu, Cd and Pb oxides when mixed with a nickel catalyst reduced its activity for this conversion, while Zn, Mn, Cr, Ce, Th, Al and Be oxides increased it. Toluene

has been identified as a product from methyl *cyclo*hexane using Al_2O_3 [19] and Cu,[24] from dimethyl *cyclo*hexane using Cu,[24] from ethyl *cyclo*hexane using Ni–Al [22] and from *cyclo*heptane using Pt on charcoal. While five-membered carbon rings offer great resistance to dehydrogenation, rings of more than six carbon atoms often undergo ring contraction under similar conditions.

Hydrocarbon Mixtures.

Dehydrogenation and cyclization have been recognized by various workers as important processes for the production of improved motor fuels. Karzhev and others [16] have aromatized Grozny aviation petrol with various catalysts such as copper chromite, chromium, chromium-molybdenum and nickel, products containing 80 per cent. aromatics being obtained in some cases.

Uranium, titanium and thallium oxides have been used as catalysts in the aromatization of kerosene.[27] More recently Koch [28] aromatized a fraction of synthetic gasoline with vanadium oxide and chromium oxide supported on alumina.

Mechanism of the Reactions involved in Dehydrogenation-cyclization.

The mechanism of dehydrogenation-cyclization is still a hypothetical matter, but some of the facts found by workers studying the fundamentals of the reactions may illuminate certain technical aspects of the conversion of non-aromatic into aromatic hydrocarbons.

Pitkethly and Steiner,[29] considering the dehydrogenation-cyclization of heptane, give evidence supporting their suggestion that heptene is an intermediate product of the reaction only in the sense that it is in equilibrium with the half-hydrogenated state. They showed that the paraffin-olefine equilibrium is not established under the conditions of their experiments, which were carried out at 475° C. over a dehydrogenation catalyst and with a contact time of 20 ± 4 seconds.

Hoog, Verheus, and Zuiderweg [30] examined a number of hydrocarbons passed over Cr_2O_3 gel at 465° C., and concluded that where the hydrocarbon structure permits of direct formation of a six-membered ring, such structures are aromatized to a large extent, but other structures are not appreciably aromatized. In the aromatization of hydrocarbon mixtures, therefore, the percentage aromatics produced by dehydrogenation-cyclization will depend on the proportion of paraffin hydrocarbons with suitable structures.

Taylor and Turkevitch [2] studied the conversion of various olefines, including 2-methyl-pentene-2, 2-ethyl-butene-1, heptene-1, heptene-3, 5-methyl-hexene-2 and octene-1, and concluded that the rate of conversion of olefinic hydrocarbons into aromatics is initially more rapid than that for saturated hydrocarbons, but that the deterioration in the activity of the catalyst is also more rapid. They suggested that this latter fact is due to the number of side reactions involved and deposition of carbonaceous material on the catalyst surface.

The Catalysts Used.

The various catalysts which have been used for the production of aromatics from unsaturateds, paraffins and naphthenes are the metals of

Group VIII (Co, Ni, Pt, and Pd), the transition metals of Groups V and VI (V, Cb, Ta, Cr, Mo, W, and U) and the oxides of the transition metals of Groups IV, V, and VI (Ti, Zr, Ce, Th, V, Cb, Ta, Cr, Mo, W, and U), either singly or in combination. Non-metals such as silica gel and activated carbon have also been shown to be active for this conversion. Various carriers have been used, and it has been suggested that carriers of any inert material are efficient if they have a large surface area. Florida earth and similar materials, after treatment with water, dilute caustic soda, ammonia, etc., are suggested for use as carriers [31] for catalysts used in the dehydrogenation of unsaturated hydrocarbons. Activated granulated alumina, however, seems to be recommended by later American workers.

The processes of ring closure of C_6–C_{12} paraffins and olefines, of course, involve dehydrogenation. In the reactions studied for pure hydrocarbons the process has been one purely of dehydrogenation-cyclization, involving essentially no scission of a C–C bond, although some decomposition usually occurred. Since it had been shown that Ni, Co and Fe were catalysts which activated the C–C bond, Taylor and Turkevich [2] suggested that these metals are of doubtful utility for maximum dehydrogenation-cyclization, and copper was rejected because of the sintering observed at about 400° C. It is worth mentioning here, however, that Adkin's catalyst, copper chromite, does not sinter readily at this temperature, and that copper chromite catalysts appear to be active in the aromatization of hydrocarbon mixtures.[16] On the basis of his own fundamental work on activated adsorption, where it had been shown that oxide hydrogenation–dehydrogenation catalysts exercise their activity at higher temperatures than the corresponding metal catalysts, and considering the thermodynamical requirements for the cyclization reaction, Taylor investigated oxide catalysts. Turkevich and Taylor [32] and Howard and Taylor [33] showed that the position of chromium sesquioxide gel for hydrogenation–dehydrogenation reactions, claimed by Lazier and Vaughen [34] to be unique, is only one of degree. They indicated that the activated adsorption of hydrocarbons on oxide catalysts is negligible below 300° C., but at higher temperatures there is definite evidence of interaction between the gases and the surface. In accordance with their general theory, these workers considered the conversion of paraffinic into aromatic hydrocarbons to involve four steps :—

(1) Activated adsorption of the paraffin on to the surface.
(2) Surface dehydrogenation with the formation of adsorbed aromatic and adsorbed hydrogen.
(3) Desorption of hydrogen.
(4) Desorption of aromatic.

The rate of conversion of paraffin into aromatic would be that of the slowest of these steps. It was concluded that chromium sesquioxide, principally, and other oxide catalysts are ideal for cyclization, and that although there is no data on the relative adsorption of aromatics and paraffins on the catalyst surface, it was assumed that the paraffins can compete effectively for the surface with the aromatics.

More recently, Taylor and Fehrer [45] have found that Cr_2O_3 and to a smaller extent Mo, Mn, Ce, and V catalysts are poisoned for aromatization

by olefines. Two-component gel catalysts of Cr_2O_3 with Cu, Ni, Pd, MnO, ZnO, MoO_2, SiO_2, ZrO_2, and SnO_2 were studied for the dehydrogenation–cyclization of *n*-heptane. The ZrO_2 and SnO_2 catalysts were superior to Cr_2O_3 alone.

Moldavski, Kamusher, and Kobyl'skaya [14] have reported that glass and silica gel are inactive, whilst ZnO, TiO_2, MoO_3, and MoS_2 are active in the aromatization of *n*-octane, and have pointed out that catalytic cracking of the higher hydrocarbons can yield either complex aromatics which lose side-chains or fragments which join together to form aromatics.

Efficient dehydrogenation-cyclization catalysts containing in order of efficacy, oxides, of the metals of Groups VI, V, and IV, have been developed by Grosse, Morrell, and Mattox,[12] minor proportions of the metals being deposited on various carriers by impregnating the carrier with a solution of a decomposable compound of the metal. Their results show that at all contact times a vanadium–molybdenum catalyst is less active than a simple chromium catalyst, but that the chromium–molybdenum and chromium-vanadium catalysts give better results at longer contact times than any of the single metal catalysts. The triple chromium–vanadium–molybdenum catalyst is found to be even more active than the double catalysts. If equal atomic proportions of the promoting metals were used in each case —and this appears to be the most reasonable way of comparing the activity of the various metals—then their results differ from those expected from a consideration of the hypothesis due to Griffith,[35] who postulated that " the optimum promoter concentration is a function of the catalyst and not of the promoter."

Work in connection with the Fischer–Tropsch process indicated that cobalt and allied metals are susceptible to poisoning by sulphur, but copper chromite catalyst has been stabilized against sulphur for hydrogenation catalysts by the incorporation of barium. Molybdenum trisulphide has been claimed as a desulphurization-hydrogenation catalyst, and sulphur itself, of course, is a dehydrogenating agent.

Taylor and Turkevich [2] found that water vapour was strongly adsorbed on chromium sesquioxide gel and was a marked poison for the cyclization reaction, but no difference in activity could be detected for heptane left in contact with water and heptane which had been dried using phosphorus pentoxide. Water appears to be a reversible poison, whereas ethylene was found to poison the catalyst irreversibly.

Much of the published work is very useful, but care must be taken in its interpretation, as different apparatus and different analytical methods used make comparative study difficult. In the present work, a small part of the published work was repeated, in order to achieve some arbitrary standard conditions necessary for a comparative chemical approach.

Thermodynamic Considerations.

As early as 1931 Frohlich observed,[36] that thermodynamic considerations led to the conclusion that all the hydrocarbons are interrelated in such a manner that it should be possible to pass from one to another almost at will.

Thermodynamic considerations indicate the temperature and pressure at which a given reaction can occur to a useful extent, but can, however, be only a general guide as care must be taken in the interpretation of thermo-

dynamic data because the values of free energy of formation, especially at the higher temperatures, are known accurately for only a very few hydrocarbons.

In 1937 Thomas, Egloff, and Morrell [37] collected most of the work that had been done on the thermodynamic properties of hydrocarbons and discussed the differences between results obtained from calorimetric measurements and those calculated from Raman and infra-red spectra. New free-energy equations were derived for straight-chain paraffins and olefines with a terminal double bond, and using these, approximate free-energy values were calculated for hydrocarbons where other data were non-existent. With the free-energy values for relevant hydrocarbons at 298° K. and 1000° K. thus collected, various reactions involved in cyclization have been considered. Thermodynamics, however, can give no indication of the rate of a reaction, and as this is often the most important factor, the course of a reaction is not indicated. But such study gives information on the temperature range in which to look for a catalyst.

The method used in the following calculations is based on the accepted relation :

$$\Delta F^\circ_T = -RT \log_e K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$K = e^{-\frac{\Delta F^\circ_T}{RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Where ΔF°_T = free energy change,
K = equilibrium constant,
T = absolute temperature.

It is obvious that if $\Delta F^\circ_T = 0$, $K = 1$, if ΔF°_T is +ve, K is less than 1, and if ΔF°_T is −ve, K is greater than 1.

When K is greater than 1, the reaction can be said to proceed to a convenient extent—*i.e.*, it is " permissible."

An approximate linear relationship, within the limits of accuracy of the free-energy data :—

$$\Delta F^\circ_T = A + BT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is assumed for the reactions considered; A and B are then calculated using the values of ΔF°_T at 298° K. and 1000° K. for standard free energies of formation from graphite and hydrogen at atmospheric pressure for the individual componants of a reaction. Equation (3) is then solved, and the temperature to give a zero value for ΔF°_T—the neutral equilibrium temperature—thus calculated.

The main assumption in the calculation is, then, that the deviations of the free-energy temperature relationships from linear are within the errors involved in the determination of the free energy values. Ewell [38] showed the significance of the neutral equilibrium temperature, and pointed out that the free energy temperature relationship is linear if the specific heat change with temperature is small. Consider the fundamental equation for a reaction at $T°$ K :

$$\Delta F^\circ_T = \Delta H^\circ_T - T\Delta S^\circ_T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Where ΔF°_T = free energy change,
ΔH°_T = heat content change,
ΔS°_T = entropy change and
$T°$ = absolute temperature.

If at $T°$ K. equation (4) represents a reaction, the free energy change involved at T_1K is given by equation (5) :—

$$\Delta F°_{T_1} = \left[\Delta H°_T + \int_T^{T_1} \Delta C°_p dT\right] - T_1\left[\Delta S°_T + \int_T^{T_1} \frac{\Delta C°_p \, . \, dT}{T_1}\right] \quad . \quad (5)$$

Where $\Delta C°_p$ = change in specific heat (at constant pressure of 1 atmosphere). Since this factor $\Delta C°_p$ would be small in the cyclization reaction, the assumption of a linear relationship between $\Delta F°_T$ and temperature is justified, for if ΔC_p is neglected, equation (5) becomes :

$$\Delta F°_{T_1} = \Delta H°_T - T_1 \Delta S°_T \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Using equations (2) and (3) and the data collected by Thomas, Egloff, and Morrell,[37] many interesting calculations of the neutral equilibrium temperature for various reactions at atmospheric pressure have been made, some of which are given in Table I below, together with the constants A and B in the equation $\Delta F°_T = A + BT$. The accuracy of the calculations depends in each case on the factor Cp and on the free-energy values.

TABLE I.

	Reaction.	Neutral equilib. Temp., ° C.	*A*.	*B*.	Conclusions.
1	*n*-Heptane to toluene, $C_7H_{16} \longrightarrow C_7H_8 + 4H_2$	283	60,700	−109	Reaction "permissible" above 283° C.
2	*n*-Heptane to *n*-heptene-1, $C_7H_{16} \longrightarrow C_7H_{14} + H_2$	610	30,900	− 35	Reaction "permissible" above 610° C.
3	Toluene to naphthalene and *iso*butene, $2C_7H_8 \longrightarrow C_{10}H_8 + C_4H_8$	—	20	+6·04	Reaction is not "permissible."
4	Toluene to naphthalene and elements, $2C_7H_8 \longrightarrow C_{10}H_8 + 4C + 4H_2$	1,355	142,300	+ 87·4	Reaction "permissible" at very high temperature.
5	*n*-Heptane to naphthalene and elements, $2C_7H_{16} \longrightarrow C_{10}H_8 + 4C + 12H_2$	199	135,500	−287	Reaction "permissible" above 199° C.
6	*n*-Heptene-1 to toluene, $C_7H_{14} \longrightarrow C_7H_8 + 3H_2$	129	29,760	− 73·8	Reaction "permissible" above 129° C.
7	Toluene to benzene and elements, $C_7H_8 \longrightarrow C_6H_6 + C + H_2$	115	9,300	−239	Reaction "permissible" above 115° C.
8	*cyclo*Hexane to benzene and hydrogen, $C_6H_{12} \longrightarrow C_6H_6 + 3H_2$	253	49,800	−947	Reaction "permissible" above 253° C.

No calculations of the actual equilibrium constants at various temperatures are given above, but these are, of course, important when considering specific reactions. The reactions with the formation of naphthalene are interesting, *n*-heptane being unstable to this compound under the conditions of cyclization reactions. In the present work naphthalene formation was found to be quite general.

Results similar to those above were obtained by Taylor and Turkevich,[2] who considered the simpler possibilities of the decomposition of hexane to form :—

(1) Paraffins and olefines.
(2) Higher paraffins and hydrogen.
(3) Higher and lower paraffins.
(4) Carbon and hydrogen.
(5) Olefine and hydrogen.
(6) *cyclo*Paraffin and hydrogen.
(7) *cyclo*Olefine and hydrogen.
(8) Aromatics (benzene) and hydrogen.

These workers came to the following conclusions : Two paraffins cannot form a higher paraffin by the elimination of a molecule of hydrogen.

In the cyclization of hexane to benzene the equilibrium is completely on the side of benzene at 327° C.

Dehydrogenation of hexane to olefine and *cyclo*hexane does not become appreciable below 527° C., but such dehydrogenation, even above this temperature, is not a serious competitor to the cyclization to benzene, since the olefinic product is unstable with respect to aromatics above 277° C.

Cracking to olefines and lower paraffins, decomposition to elements, and disproportionation are all serious competitors to cyclization. Generally, it may be concluded that the possibility of conversions of straight-chain paraffins, branched-chain paraffins, olefines, and naphthenes to aromatics expected on the basis of the low energy resonance structure of the benzene ring is indicated in many cases by thermodynamic calculations, but other reactions involving the splitting of C–C bonds are serious competitors. To prevent undesirable reactions it seems, therefore, that for the aromatization of single compounds a catalyst which activates the C–H bond only should be used.

Cyclization of Hydrocarbon Mixtures.

In preliminary runs a chromium sesquioxide catalyst prepared from chromic acid deposited on Floridin was found to have little effect, while a similar catalyst prepared from chromium nitrate was much more active for cyclization. The activity of these catalysts, however, was considerably increased by using activated alumina as the carrier.

Experimental Method.

The apparatus used consisted essentially of a constant rate of delivery burette, a catalyst tube, a receiver, and a gas meter. The feed was introduced through a mercury seal, the catalyst tube heated in an electric furnace, and the receiver cooled in ice-salt. To observe the temperature of the electric furnace a pyrometer accurate to $\pm$ 5° C. at 350° C. was used. The catalyst was held in position in the tube by glass wool and broken glass. In order to avoid unnecessary cooling of the catalyst and because of the endothermic nature of the reactions, a preheater was introduced, and this vaporized the liquid feed at about 400° C. To facilitate the introduction of

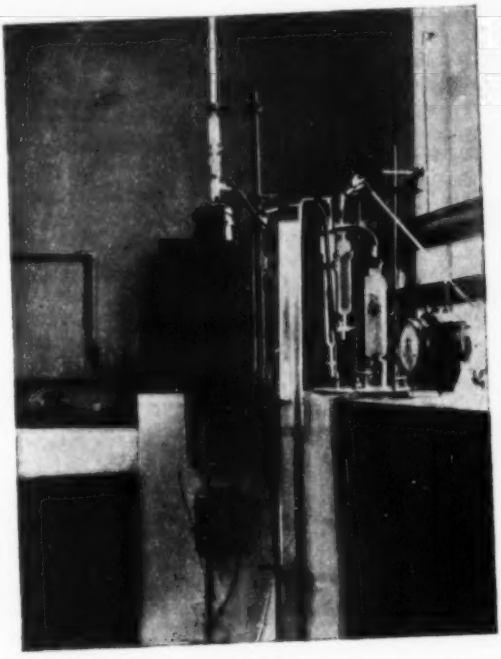

FIG. 1.

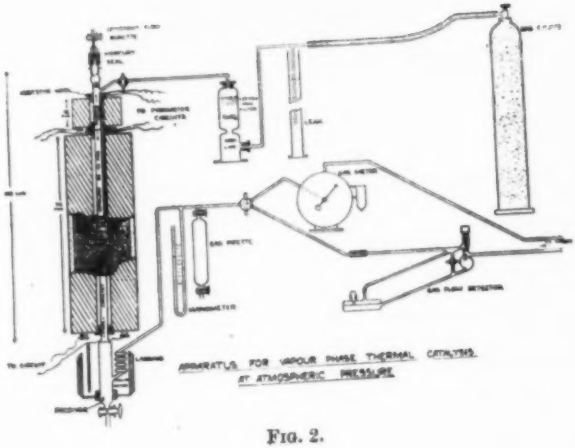
APPARATUS FOR VAPOUR PHASE THERMAL CATALYSIS
AT ATMOSPHERIC PRESSURE

FIG. 2.

gases into the catalyst tube the end of the tube was fitted with a ground-glass joint and interchangeable stoppers.

Although there was a slight directional slope on the catalyst tube, the liquid charge remained in contact with the broken glass in the preheater long enough in some cases partly to decompose and deposit tar.

Later the apparatus was modified and the catalyst tube placed in the vertical position, in order to decrease liquid contact time in the preheater and to facilitate continual removal of the product with the receiver at the lower end of the catalyst tube; for the connection of catalyst tube and receiver it was found advisable to use a mercury seal. A manometer was fitted and a sensitive flowmeter used as a gas detector. This flowmeter

CONSTANT FLOW BURETTE

FIG. 3.

was not used to measure the gas produced, and by-passes were introduced for connecting a gas-meter or absorbing bottles when necessary. The apparatus is shown in Figs. 1 and 2.

THE CONSTANT-FLOW BURETTE.

The constant-flow burette is shown in Fig. 3. When the tap in A is closed and liquid is run from the burette, a partial vacuum is developed in A. The pressure in A being, (Atmospheric $- ac \times \rho$) inches of water.

where c = level of liquid in burette bulb,
a = level of liquid in tube—*i.e.*, at the bottom of the inner tube for constant flow,
ρ = density of liquid.

The driving head is then *ab*, and there is a constant resistance to flow at *B*. Hence, since *a* is at atmospheric pressure, the flow will be constant for any setting of *a*, if pressure at *b* is constant.

Three notable disadvantages of this burette in the present work are: first, the necessity for a filter to prevent interference with the capillary; second, the rate of flow depends on the pressure at *b* and hence varies with the gas formed in the catalyst tube, and third, the rate of flow depends on the density of the charge. Again, the rate of flow cannot be measured while a run is actually in progress.

Attempts were made to eliminate errors due to back pressure by connecting the upper part of the catalyst tube with the sliding tube of the burette, and thus making the pressure at *a* and *b* equal in all circumstances. These attempts failed because of condensation of vapours in the connecting tube.

It was found, however, that although the back-pressures were different for different reactions, that during short runs the back pressure was nearly constant, and consequently the rate of flow was constant. The actual rate was then found from the total liquid passed and the duration of the run. It was not possible, then, to use exactly the same rate of charge for all experiments, but conditions were approximately the same in most cases.

The Standard Conditions.

For a comparative study of the reactions of various hydrocarbons and mixtures some standard conditions were required. It was not required that these conditions should be the best possible obtainable for any particular aromatization reaction, but that the conversion should proceed to a reasonable extent. The arbitrary conditions chosen were therefore not the best possible conditions for the aromatization of any particular hydrocarbon. By controlling conditions as near to " Standard " as possible, experiments made using different apparatus were made comparable.

The liquid space velocity was 0·33 c.c. of liquid per c.c. of catalyst per hour.

The liquid products were cooled at $-5°$ to $-14°$ C., and vapours which passed through a condensing spiral at this temperature range were measured as gas. The preheater temperature was controlled at 250–300° C.

Preparation of the Molybdenum Catalyst.

20 grams of A.R. ammonium molybdate were dissolved in 100 grams of 0·800 A.R. ammonium hydroxide and an equal volume of water. This solution was poured slowly on 250 grams of Grade A activated alumina 8–14 mesh (Alorco) which had been heated at 350° C. for 3 hours and cooled in a vacuum desiccator without desiccant. The mass was stirred for about 30 minutes when the solution was completely and uniformly absorbed by the alumina. This was dried at 100° C. for 1 hour and then left overnight at 310° C. $\pm$ 10° C. The catalyst was introduced into the reactor and reduced by passing a stream of dry hydrogen for 3 hours at 350° C., and then remaining hydrogen was swept away with nitrogen. It was shown that for short runs the temperature of reduction of the catalyst did not effect the cyclization reaction of *n*-heptane. The unpromoted catalyst thus prepared contained 2 per cent. molybdenum, and was in a very convenient and stable form.

The catalyst was regenerated by sweeping out any hydrocarbons with nitrogen, switching off the furnace, and then passing dry air with the preheater at 550° C. until the carbonaceous deposits on the catalyst had been reduced. Remaining air was then swept out with nitrogen, and hydrogen passed for 3 hours to effect reactivation by reducing the molybdenum oxides.

Analytical Method.

A 25 theoretical plate packed column and laboratory distillation unit for distillation of volumes of the order of 500 c.c. was constructed for preliminary distillations.

Chemical Analysis for Aromatics.

When only approximate indication of composition was required, the aromatics were estimated by aniline-point determinations before and after absorption with 98 per cent. sulphuric acid, following the removal of the unsaturateds by absorption in 80 per cent. sulphuric acid. Nitration methods appear preferable, however, where more accurate knowledge is required and, because of the small volumes available from fractional distillation, the method of Manning and Shepherd [39] was examined. Their method consists in passing a stream of air over the hydrocarbons and absorbing the aromatic and unsaturated vapours in a nitrating mixture. The weight of the aromatics and unsaturateds is thus obtained and the percentage paraffinic material found by difference. The nitrating solution is heated to 100° C. to complete the nitration, during which treatment the unsaturateds are oxidized to form products soluble in water or caustic soda solution. The nitrated aromatics are extracted with benzene, which is removed by distillation, and the weight of the original aromatics is estimated from the weight of the nitro-compounds. These workers found the method gave results correct to within $\pm$ 0·1 per cent. for mixtures containing 4·4, 18·4, 48·5 per cent. benzene.

In the present work, for the mixtures containing 10–60 per cent. benzene or toluene and a maximum of 30 per cent. unsaturateds the method was found to be accurate to $\pm$ 1 per cent. The estimation of aromatics was not high if the nitro-compounds were dried for a few hours in a vacuum desiccator. For high-percentage unsaturateds accurate results could not be obtained even when an additional absorber containing 70 per cent. sulphuric acid was introduced as recommended by Manning and Shepherd. A comparison of the results obtained by extraction of the nitro-compounds after pouring the nitrating mixture into ice-cold water with those obtained by separating directly after the same treatment and cooling for several hours through a tared sintered-glass Gooch crucible, showed differences of the order of 1 per cent. on the whole mixture for the estimation of benzene and toluene. The second method of separation of the nitro-compounds also gave pure crystalline products (dinitrobenzene and trinitrotoluene), which were easily dried, and in many cases their purity was not measurably improved by recrystallization. When the nitro-compounds were extracted, however, the products were usually less pure, and their melting points were increased on recrystallization. The Manning–Shepherd absorption train was proved quite successful for the hydrocarbon mixtures similar to benzole,

and finally the modified absorber due to Gooderham [40] was introduced. The method selected was, in general, that of distillation and fractionation followed by estimation of aromatics, unsaturateds and paraffinics by the absorption-train method supplemented by examination of the nitrated aromatic compounds and further examination when necessary. Naphthenes were generally negligible throughout.

Estimation of the Unsaturateds.

The most usual method for the estimation of unsaturateds is by bromine absorption with estimation of the molecular weight from the distillation range on the assumption that only aliphatic mono-olefines are present. Hoog, Verheus, and Zuiderveg [30] used this method in similar catalytic cyclization work, followed by removal of the unsaturateds with thioglycollic acid in a homogeneous propionic acid solution at room temperature prior to the estimation of the aromatics by absorption in 98 per cent. sulphuric acid. Treatment with thioglycollic acid can be used for the estimation and isolation of the unsaturateds, but the cost of the reagent in this country is prohibitive.

The determination of bromine numbers for hydrocarbon mixtures was studied in some detail.[41] The evidence obtained suggested that bromine absorption cannot be used to estimate the actual percentage unsaturateds present in complex mixtures, although, using the titration technique of Lewis and Bradstreet,[42] it is possible to find quickly a value for comparative purposes. For the normal mixtures met with in this work the absorption train gives satisfactory results for the estimation of unsaturateds, although it gives no indication of their qualitative composition. The method selected for unsaturateds was therefore absorption train analyses supplemented when necessary by bromine-number determinations.

Estimation of Paraffins and Naphthenes.

Paraffins and naphthenes were estimated together in the absorption train, but the production of naphthenes has not been observed during cyclization reactions, and generally analysis for naphthenes was not made, although by the introduction of a cooled trap in the absorption train it was found possible to collect small samples of paraffinic constituents for further examination.

Determination of Sulphur.

The hydrocarbon mixture was introduced into a Matheson–Cook bomb calorimeter over 30 c.c. of water and ignited in oxygen to produce sulphur trioxide, which dissolved. The sulphuric acid thus formed was isolated from any other acids, such as CO_2 and HNO_3, which might be present by precipitation as benzidine sulphate, which was then hydrolysed at 50° C., and the acid solution titrated with standard potassium hydroxide.

Gas Analysis.

Hydrogen, carbon dioxide, and the hydrocarbons were determined using the Bone and Wheeler apparatus.

Sulphur dioxide in regenerating gases from the catalyst tube was not estimated, but was detected by a dilute solution of *p*-rosaniline. Hydrogen

sulphide in the gases from sulphur runs was estimated by absorption in 2N aqueous sodium hydroxide and back-titration with standard iodine and sodium thiosulphate solution after acidifying with hydrochloric acid.

Cyclization of *n*-Heptane.

The *n*-heptane used had the following characteristics: refractive index n_D^{20}, 1·38775; density, D^{20}, 0·6836; boiling range, 98–98·5° C.; freezing point, — 90·7° C.

Six preliminary runs were made on heptane. Two of these, when an approximately 6 atomic per cent. chromium sesquioxide was used as the catalyst at 500° C., with a liquid-space velocity of 1·3 c.c./c.c./hr., yielded a liquid containing 60 per cent. toluene. In another run using the same chromium catalyst the space velocity was very much lower, but the toluene in the liquid product was still about 60 per cent. This result is in agreement with the results of Groose, Morrell, and Mattox, who used this catalyst and concluded that space velocities lower than about 0·3 c.c./c.c./hr. do not appreciably improve the percentage yield of toluene. The preliminary runs where the lower percentage molybdenum catalyst was used did not show very different results from these for the chromium catalyst. No conclusions on the effectiveness of the catalysts were reached from this, however, because the preparations were not made under strictly identical conditions.

Using the standard conditions referred to above, 250 c.c. of *n*-heptane were passed over the standard molybdenum catalyst at 550° C.

Products: Gas and carbon: the gas was assumed to be a mixture of methane and hydrogen on the basis of other published work, and the carbon was deposited on the catalyst. 93 per cent. of the charge was a pale yellow liquid which analysed :—

Naphthalene 1 per cent.
Toluene 55 per cent.
Unsaturateds 5 per cent.
Heptane 40 per cent.
Overall conversion to toluene = 53 per cent.

The Effect of a Mild-Steel Catalyst Tube.

Observations on the effect of a mild-steel catalyst tube on the cyclization of *n*-heptane were inconsistent, and are not therefore reported in detail. There are certain general conclusions which can be made, however, from over 100 runs in mild-steel tubes.

(1) Mild steel effects the cyclisation reaction.
(2) A new tube enhances the reaction.
(3) After some time the oxide-sulphide scale must be removed before each run to achieve consistently good results.

Cyclization of Heptene.

Since pure heptenes were difficult to obtain and the present work was concerned mainly with the cyclization of hydrocarbon mixtures, technical heptene was used in the experiments described below.

The technical heptene used had a bromine number of 165 (163 for pure heptene), although the distillation curve indicated only 80 per cent. *n*-heptenes.

285 grams of technical heptene were passed over the molybdenum catalyst under the standard conditions and at 550° C. The products are indicated :—

(1) 5 grams of " tar " was deposited in the catalyst tube, extractable with petroleum ether.

(2) A black deposit on the catalyst was formed which was not extractable with organic solvents and was therefore assumed to be carbon.

(3) 65 litres of gas were produced, a sample of which was analysed.

Gas Analysis		
	CO_2	Nil
	Olefines	44 per cent.
	Oxygen	Nil
	CO	6 per cent.
	Hydrogen	10 per cent.
	Paraffins	40 per cent.

(4) 185 grams of dark yellow liquid which was distilled, fractionated and analysed for unsaturateds, aromatics and paraffinic hydrocarbons.

In the analysis of these fractions the absorption train method did not give consistant results even with an additional absorber containing 70 per cent. sulphuric acid to remove most of the unsaturateds. The aromatics produced were difficult to nitrate quantitatively, and the products required recrystallizing. The unsaturateds were therefore estimated from the bromine numbers of the fractions, the aromatics by using these values for unsaturateds, and the paraffins were estimated by difference. These results are summarised in Table II.

TABLE II.

Product from Cyclization of Heptene.

	Fraction, ° C.	Per cent. of liquid product.	n_D^{20}.	Aromatics, per cent.	Unsats., per cent.	Paraffins, per cent.
I	67–86	19	1·4310	20	34	47
II	86–93	18	1·4800	20	34	46
III	93–96	34	1·4550	27	38	35
IV	96–110	16	1·4220	15	39	47
V	110–187	10	1·4740	30	17	53

In the first four fractions the aromatics were toluene and benzene, but in fraction V were probably toluene and xylenes, as the recrystallized nitro-compounds melted at 157° C.

Conversion Data.

Charge to aromatics	14 per cent.
Charge to paraffins	19 „ „
Charge to tar, carbon, gas, and loss	38 „ „

From a consideration of these results it appears that benzene, toluene, and xylenes were produced and the percentage aromatics in the liquid product was about 22 per cent. There is considerable loss by decomposition in the catalytic treatment of technical heptene, and a spreading of the distillation range of the liquid product is obtained. In Fig. 4 are shown the distillation curves of technical heptene and the product. Some polymerization occurs, and, because this is indicated, the percentage unsaturateds in Fraction V as calculated from the bromine number may be too low. A factor which might account for the low yield of toluene from the technical heptene is that some of this was heptene-3, which would be more stable than the less symmetrical heptenes under the conditions of the reaction. The considerable production of paraffins is surprising, but these are not produced mainly by cracking or by disproportionation, because these saturateds are present in similar proportions in all the fractions. Because of

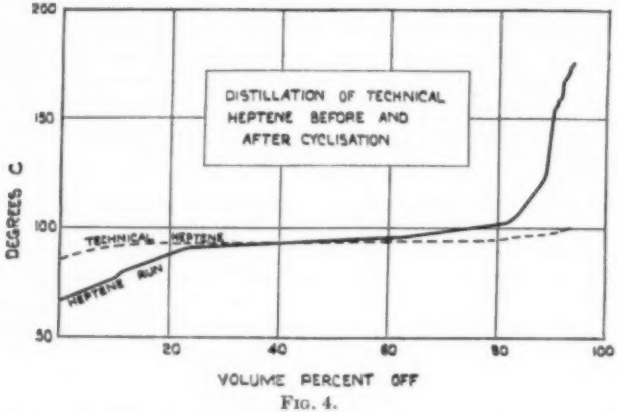

FIG. 4.

this production of paraffins some confirmatory analyses were made. The original heptene was examined further, and found to contain negligible paraffins. A sample of the heptene product was completely brominated, washed free from bromine, and the product distilled from the bromo-compounds and separated into three fractions. The composition of these fractions was then estimated approximately, by an aniline-point method. The percentage paraffins indicated in this way are shown in Table III below.

TABLE III.

Paraffins in converted Heptene.

Fraction, ° C.	Paraffins, per cent.
<100	52
100–103	40
103–114	41

Although these results in themselves cannot give an accurate estimate of the composition of the product, the previous analysis is confirmed, and there

is little doubt that considerable hydrogenation of technical heptene to paraffins accompanied dehydrogenation, cyclization, and cracking under the conditions described.

Heptane–Heptene Mixtures.

The effect of unsaturated hydrocarbons in the substrate on the cyclization properties of paraffins was observed by using various mixtures of *n*-heptane with technical heptene under the standard conditions and at 550° C. The results are shown in Table IV.

TABLE IV.

Cyclization of Heptane–Heptene Mixtures.

Heptene in charge, per cent.	Product.			Aromatics in unsaturateds-free, per cent.
	Unsaturateds, per cent.	Aromatics, per cent.	Paraffins, per cent.	
10	6	24	72	25
19	15	22	59	26
36·8	35	—	—	30
60	52	—	—	33
80·6	72	11	17	39
100	82	10	8	57

In each case carbon and gas were produced in approximately equal quantities, although noticeably more tar was produced for the more un-

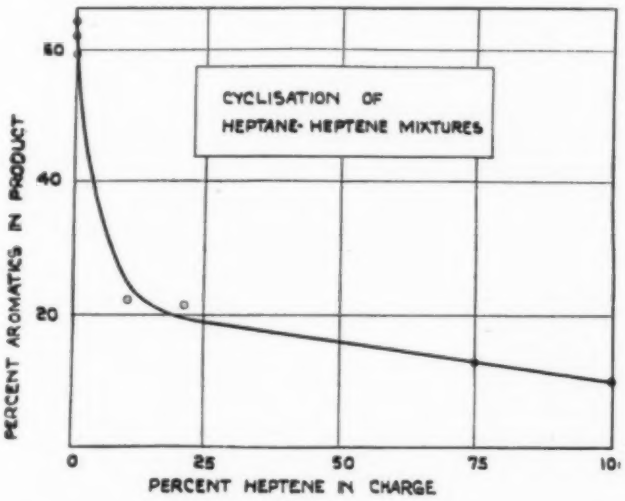

FIG. 5.

saturated feed stocks. When the results are plotted graphically (Fig. 5) it is seen that cyclization decreases with increase in the heptene content of

the charge, although some of the heptene is converted into aromatics or paraffinic hydrocarbons in each case. It appears also that the percentage aromatics in the product falls off rapidly with initial increasing heptene in the feed.

Stability of Toluene under Cyclization Conditions.

Toluene was examined under the conditions of cyclization reactions. A few preliminary runs with A.R. toluene showed a change in colour, odour, and refractive index. 1200 c.c. of pure toluene was therefore prepared, boiling at 110° C. by distillation of A.R. toluene. The toluene was passed over the molybdenum catalyst at 500° C. under the standard conditions described. The horizontal catalyst tube apparatus was used and the run was several days duration, during which time the catalyst was regenerated, and reactivated after every 3 hours.

Products :—The gas produced was analysed but was not measured.

Analysis :—	Olefines	11 per cent.
	Hydrogen less than . . .	2 per cent.
	Paraffins ($n = 1{\cdot}1$) . . .	85 per cent.

There was some indication of decomposition in the preheater, but the deposit on the catalyst was not extractable with organic solvents, and was therefore assumed to be carbon.

1130 c.c. of a pale yellow liquid was obtained which was distilled using the 25 theoretical plate still, fractionated, and analysed. The analysis is shown in Table V.

TABLE V.

Product from Thermal Catalytic Treatment of Toluene.

	Volume, per cent.	Distillation range, ° C.*	Toluene, per cent.	Unsats., per cent.	Paraffins, per cent.
I	6·4	97–109·	78	10	12
II	82·4	109–109	100	0	0
III	2	109–109	100	0	0
IV	6	109–109·5	100	0	0
V	3·2	109·5	—	0	0

* = uncorrected.

Total Analysis : 97 per cent. Toluene
1–2 per cent. Unsaturated Hydrocarbons.
1–2 per cent. Paraffin Hydrocarbons.

Toluene is thus relatively stable under the conditions described, but about 6 per cent. decomposition occurs and a small percentage of unsaturateds is definitely formed. No paraffins were isolated from the liquid product, but both paraffins and olefines were found in the gas produced.

Cyclization of Heptane–Toluene Mixtures.

The effect of the initial aromatic content of the substrate on the aromatic content of the liquid product in the cyclization of hydrocarbon mixtures was investigated for heptane–toluene mixtures.

The runs were all made at 550° C. under the standard conditions described,

excepting that deviations from the liquid space velocity of 0·3 were unavoidable, as the rate of feed varied slightly with the density of the charge. The gas produced was not measured. The results are shown in Table VI.

TABLE VI.

Cyclization of Heptane–Toluene Mixtures.

Toluene in charge, per cent.	Overall heptane converted, per cent.	Liquid product.			
		Per cent. on charge.	Unsats., per cent.	Paraffins, per cent.	Aromatics, per cent.
100	—	69	0·4	0	99
96	0	67	0·5	0	99
92	0	68·3	0·5	0	99
83·5	0	75·8	0·6	0	99
65·6	0	72·1	0·7	16	83
46·0	25·8	77·9	1·6	18	80
24·1	52·6	79·1	1·4	18	81
0	59·5	91·5	4·8	33	62

It appears from the results in Table VI that the total gas, carbon, and tar formation was greater for higher percentage toluene charges. Parallel

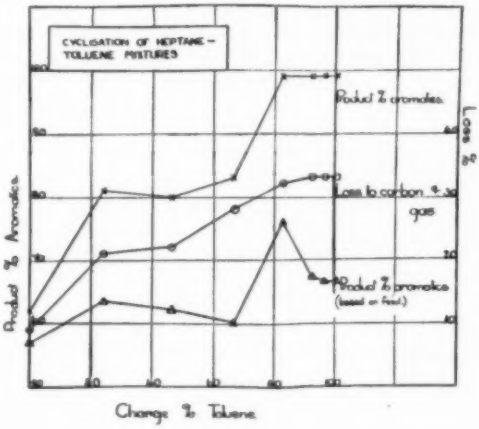
CYCLISATION OF HEPTANE – TOLUENE MIXTURES
Product % aromatics
Loss %
Loss to carbon & gas
Product % aromatics (based on feed)
Product % Aromatics
Charge % Toluene

FIG. 6.

with this is the fact that less unsaturateds were formed from these charges. Although the same catalyst was used for the runs and was regenerated and reactivated before each run, the increased loss to carbon, gas, and tar cannot be due to the incomplete removal of carbon and its consequent catalytic cracking activity, as the runs were made in the order shown, and this effect, like that of any deviation in liquid-space velocity (due to the densities of the charges), would be opposite to the results found. Again, although the losses were phenomenally great for the pure toluene charge, the general tendency for increased conversion losses with increasing toluene in the

charge is still shown by the results in Table VI if this run is neglected. From Fig. 6 and Table VI it is apparent that for the most economical conversion of *n*-heptane at 550° C. the least aromatic charge is desirable, while for the production of highly aromatic products, however, there is an optimum range for the aromatics in the charge. It appears, then, that at 550° C. two types of processes are active, cyclization and thermal aromatization or cracking.

Although in the 65·6 per cent. and 83·5 per cent. toluene runs there was no overall conversion of heptane into toluene, since from the general results in Table VI the aromatics are lost to gas, carbon, and tar rather more readily than the paraffins, it seems that heptane was converted into toluene in predominantly aromatic mixtures.

Cyclization of 2 : 2 : 4-*Trimethyl Pentane.*

Hoog, Verheus, and Zuiderweg [30] compared the cyclization of various paraffins over pilled Cr_2O_3 catalyst with contact times of 18–24 seconds and a reaction temperature of 465° C. Eighteen hydrocarbons were examined, and of these, *n*-pentane, 2-methyl pentane and 2 : 2 : 4-trimethyl pentane were not appreciably aromatized, although in each case there was considerable olefine formation, but no notable cracking. From distillation data and the composition of reaction gases it was deduced that the formation of higher-molecular-weight compounds occurs with these base materials which are not appreciably aromatized (*e.g.*, 2 : 2 : 4-trimethyl pentane). It was also generally concluded that paraffins with structures not readily permitting the formation of a six-membered ring are not appreciably aromatized, and that, since there are formed from paraffins only those aromatics which would be expected on this basis, then under the given conditions chromium sesquioxide does not effect isomerization of the carbon skeleton, although some lower aromatics might be formed as a result of cracking reactions.

For the aromatization of many hydrocarbon mixtures these conclusions impose definite theoretical restrictions, and the thermal catalysis of 2 : 2 : 4-trimethyl pentane was therefore investigated further. Although the following experimental work was carried out merely to find the conditions of formation of aromatics, no single process was being studied, and no gas analyses were made, certain interesting facts were found.

Experimental.

(1) Pure 2 : 2 : 4-trimethyl pentane twice redistilled from the Röhm-Haas product was passed over the molybdenum catalyst at 550° C., using a mild steel catalyst tube and a liquid catalyst-space velocity of about 0·3 c.c./c.c./hr. A pale yellow liquid product was obtained, 50 per cent. of the charge. There was considerable gas and carbon production.

Analysis of Liquid Product.

Aromatics	. . . . .	50	per cent.
Paraffins	. . . . .	47	,, ,,
Naphthalene	. . . . .	2	,, ,,
Unsaturateds	. . . . .	1	,, ,,

There was, then, a conversion of 25 per cent. of the charge into aromatics. The nitro-compounds prepared from the aromatics at 100° C. melted at 179° C. That these were aromatic compounds was shown by reduction to amines, diazotization, and coupling with β-naphthol. Oxidation of the original hydrocarbon mixture with alkaline permanganate yielded some phthalic acid, m. p. 190° C. The aromatics in the product were then a mixture of xylenes, *o*-xylene being identified.

(2) 166 c.c. of pure 2 : 2 : 4-trimethyl pentane were passed over a 6 atomic per cent. chromium sesquioxide alumina catalyst at 450° C. in a mild-steel catalyst tube. The catalyst was prepared from chromium nitrate and reduced in hydrogen. The liquid catalyst space velocity was 0·33 c.c./c.c./hr. 18·5 litres of gas and a pale yellow liquid (89 per cent. of charge) were produced.

Analysis of Liquid Product.

Aromatics	1·9 per cent.
Unsaturateds :	15·1 „ „
Paraffins (by difference) :	82 „ „
Gum (including some naphthalene) : less than .	1 „ „

Considering the nitro-compounds obtained the aromatics present were probably mixed xylenes together with some benzene. Identification by oxidation with alkaline permanganate was not successful.

The unsaturateds were not identified. The aromatics and unsaturateds were then removed by absorption in 98 per cent. sulphuric acid and the residue examined; distillation indicated that the greater part of the residue boiled below 84° C. and that there was a 10 per cent. fraction at 74° C. The refractive indices of various arbitrary fractions were found, and some are shown in Table VII. From these results it appeared that isomerization

TABLE VII.

	Fraction, ° C.	Per cent. of aromatics and unsats.-free product.	n_D^{20}.
(1)	64	15	1·3900
	64–85°	35	1·3919
	85–98	20	1·3945
	Residue	6·5	1·4362
	Original mixture	100	1·3979
(2)	40	6	1·3935
	40–50	2	
	50–74	38	
	74	26	—
	74–98	18	1·3948
	Residue	—	1·4185

to more highly branched compounds had taken place. However, although 98 per cent., sulphuric acid was shown not to affect "*iso*-octane" alone, it was found that under the usual conditions washing with acid of this strength does not remove unsaturateds completely, and that the effect of acid treatment in the presence of such unsaturateds could account completely for the results found.

The production of both lower- and higher-molecular-weight compounds was indicated, and further evidence for the former was obtained by determination of molecular weights of two fractions from a further distillation. This is shown in Table VIII.

TABLE VIII.

Sample.	Molecular weights.	
	Found.	Theoretical.
Original 2 : 2 : 4-Trimethyl pentane . .	112	114
70–90° C. Fraction	102	100 for C_7H_{14}
90–112° C. Fraction	112·1	114 for C_8H_{16}

From the above it would appear that considerable aromatization of 2 : 2 : 4-trimethyl pentane is possible under certain conditions, but is accompanied by very considerable cracking.

Benzene-2 : 2 : 4-Trimethyl Pentane Mixture.

From thermodynamic considerations it has been shown that the reaction of benzene and 2 : 2 : 4-trimethyl pentane to give toluene and the elements is permissible in the temperature range of the cyclization reaction. From this indication and from a consideration of the cracking possibilities, alkylation of the aromatic ring with a dehydrogenation catalyst might take place under suitable conditions.

A mixture of 55·8 per cent. pure thiophen-free benzene and 44·2 per cent. of pure 2 : 2 : 4-trimethyl pentane was passed over the molybdenum catalyst at 550° C. under the standard conditions described above. The product was distilled, fractionated and analysed.

Products.

10 per cent. of charge as gas, carbon, and loss.

90 per cent. of charge as a colourless liquid with a distillation range of 74–110° C. (The distillation range for the charge was 80–95° C.)

Analysis.

The analysis of the product is shown in Table IX.

TABLE IX.

Analysis of Fractionated Liquid Products from Benzene-iso-octane Run.

	Fraction, ° C.	Volume, per cent.	Refractive index, n_D^{20}.	Unsats., per cent.	Aroms., per cent.	Paraff., per cent.	M. p. of nitro-compounds, ° C.
1	74–80	8	1·4905	98	58	32	88
2	80–83	45	1·4697	18	50	32	86
3	83–90	26	1·4554	29	35·1	35·0	87
4	90–110	6	1·4700	10	49	4	179

The aromatics in fractions 1, 2, and 3 were assumed to be benzene from the melting points of the isolated nitro-compounds. The aromatics in

fraction 4 were probably *o*- and *m*-xylenes. The nitro-compounds isolated from this fraction were reduced, but the amines could not be isolated satisfactorily. On diazotization, however, a dye was obtained by coupling with alkaline β-naphthol. Neither the diazo-dye nor the amine hydrochloride could be crystallized satisfactorily for characterization.

The total liquid product had the following composition.

48 per cent. aromatics.
40 per cent. benzene.
8 per cent. mixed xylenes.
35 per cent. paraffins.
15 per cent. unsaturated hydrocarbons.
0·1 per cent. naphthalene.

Thus both the percentage benzene and 2 : 2 : 4-trimethyl pentane had decreased. The reaction must have involved the benzene present, since benzene alone under the same conditions was not changed. Since, however, the formation of xylenes was found when *iso*-octane alone was treated under the same conditions, the possible alkylation of benzene with other hydrocarbons by contact catalysis is not decided either way by these results. Benzene alone was stable under the same conditions as shown by the experiment below.

Benzene Run.

Pure thiophen-free benzene was treated under the standard conditions described at 550° C.

Products.

Gas : 1 per cent. of charge. The gas did not contain unsaturateds.

Carbon : A light deposit on the catalyst unextractable with organic solvents. This deposit was noticeably less than in other runs.

Liquid : 98 per cent. of the charge as a colourless liquid boiling at 80–81° C.

Bromine number = 0
$n_D^{20} = 1{\cdot}5012, 1{\cdot}5013$
Original benzene : $n_D^{20} = 1{\cdot}5011, 1{\cdot}5010.$

Discussion.

The production of the considerable proportion of paraffinic hydrocarbons during the cyclization of technical heptene is rather surprising. Taylor and Turkevich [2] using small quantities of gel catalyst (15 g.) found that the percentage paraffins produced in the cyclization of heptene-1 dropped from 13 per cent. at 424° C. to 2 per cent. at 474° C. Since the paraffins are in similar proportion in all fractions of the product, it appears that they are produced by catalytic hydrogenation during the dehydrogenation reactions. Thermodynamically the conditions were favourable for heptene production, and the fact that this was realized to a considerable extent suggests that the conditions approached hydrogenation equilibrium conditions closely.

In Fig. 5 for heptane-heptene mixtures it is apparent that aromatization of heptane is decreased considerably by small quantities of technical heptene, and the initial presence of unsaturated compounds in the sub-

strate thus considerably limits the efficacy of the cyclization reaction. This seems to be in accordance with the discovery [2] that cyclization catalysts are poisoned irreversibly by ethylene. The conversion of heptane into toluene even in predominantly aromatic mixtures favours the assumption made by some workers that paraffins can compete effectively with aromatics for the catalyst surface under cyclization conditions.

Much more experimental work is necessary before any general conclusions can be made on the isomerization of 2 : 2 : 4-trimethyl pentane by cyclization catalyst, and the work is being continued. It seems desirable that more attention should be paid to the paraffinic portion of the products and that the formation of aromatic hydrocarbons should not be taken as the only indication of isomerization. For this purpose much greater volumes of the substrate must be used than hereto and attention given to the qualitative nature of the products.

Cyclization of Mixtures containing Sulphur Compounds.

Preliminary investigation was carried out on mixtures containing varying proportions of sulphur compounds from two aspects. The resistance to poisoning by sulphur and the desulphurization capacity of the cyclization catalysts was tested together with the effect on the chemical composition of the products from sulphur containing charges.

Experimental.

Molybdenum and chromium, forming stable sulphides, might be expected to act as desulphurizing catalysts. Indeed, molybdenum trisulphide has been claimed as a desulphurizing catalyst (B.P. 315,439) when supported on charcoal and other carriers. The trisulphide was therefore precipitated on active charcoal and dried at 110° C. With this catalyst a 30 per cent. reduction in total sulphur for a single pass was obtained running a benzole fraction with hydrogen at 300° C. On the basis of several experiments it appeared that for best results the catalyst should be treated with hydrogen sulphide at intervals. A catalyst was prepared by depositing MoS_3 and Co_2O_3 on pumice in their molecular proportions and treating with hydrogen sulphide at 300° C. At this temperature reductions in total sulphur of a benzole fraction of 14 per cent. when using a liquid catalyst space velocity of 1·9 c.c./c.c./hr. and 26 per cent. when using 0·13 c.c./c.c./hr. were obtained. In this preliminary work hydrogen was passed with the feed to reduce the sulphur compounds to hydrogen sulphide. When considering cyclization catalysts, however, it was apparent that a new principle might be involved, since the hydrogen required to reduce the sulphur compounds could be supplied, under suitable conditions, by the cyclization reaction itself. In order to test the capacity of the cyclization catalysts for desulphurization and their resistance to sulphur poisoning in a suitable time, a search was first made for the highest percentage sulphur in the charge which could be desulphurized efficiently. The conditions used were very similar to the standard conditions described above, deviations from these being due to variations in the feed-rate probably caused by increasing density of the feed with increasing content of carbon disulphide. This material was used in a 110–120° C. benzole fraction to give charges of various sulphur contents.

In Table X the experimental results are shown and in Fig. 7 are expressed graphically.

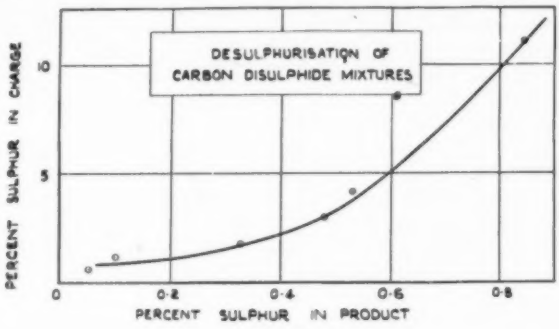

FIG. 7.

TABLE X.

Desulphurisation of Carbon Disulphide Mixtures.

Temperature : 550° C.
Contact Time : 35–40 seconds.

Run no.	Input, c.c.	Feed-rate, c.c./min.	Product, c.c.	Gas produced, c.c.	Sulphur in feed, per cent.	Sulphur in liquid product, per cent.	Desulphurization, per cent.
47	40	1	33	3200	1·14	0·10	91
48	35	0·875	32	2600	1·7	0·33	80
49	35	0·875	30	2400	3·0	0·49	84
50	34	0·875	30	2200	4·2	0·53	87
51	35	0·875	30	3200	11·2	0·85	93

The catalyst was regenerated with air before each of the runs above until no more sulphur dioxide (detected with *p*-rosaniline) was evolved. In this way, sulphur dioxide was found to be present even when air had been passing for 3 hours. When hydrogen was passed to reduce the oxide, H_2S was formed, indicating that sulphur was combined on the catalyst. H_2S and SO_2 were not estimated in the presence of each other, for it was assumed that the reactions shown would go to completion above 500° C.

Excess SO_2 . . .	$SO_2 + H_2S \longrightarrow S + H_2O$
Air	$S + O_2 \longrightarrow SO_2$
Excess H_2S . . .	$SO_2 + H_2S \longrightarrow H_2O + S$
Hydrogen . . .	$S + H_2 \longrightarrow H_2S$

The products of runs 47–51 were examined for aromatics and unsaturateds. In Table XI it can be seen that the percentage unsaturateds increases with increasing sulphur content of the charge. Although this increase is small, it is significant that the aromatic content of the product falls over a similar range. The true conversions were certainly greater than indicated in Table XI because the experimental losses were great as small volumes of the order of 100 c.c. were used.

TABLE XI.

Run no.	Charge S, per cent.	Per cent. unsats. in product.	Per cent aromatics in product.	Overall percentage conversion to aromatics.
47	1·14	12·1	80·8	2
48	1·70	14·2	78·3	7
49	3·00	13·8	79·8	3
50	4·20	15·0	76·7	1
51	11·20	17·4	76·7	1

Catalyst Desulphurization Tests.

In order to test the catalyst a long run was made charging 25·3 per cent. sulphur (as carbon disulphide) in a 110–120° C. benzole fraction.

The conditions described above were used, and samples of the product were taken at intervals. At somewhat longer intervals the hydrogen sulphide in the gas was estimated.

The catalyst was then reactivated and further charge passed. It was obvious that copious evolution of hydrogen sulphide was taking place in the second stage, but no estimations of the gas could be made. During the reactivation, however, considerable sulphur dioxide was evolved when air was passed over the catalyst.

In Tables XII and XIII are shown the results for the first and second stage runs.

TABLE XII.

Desulphurization—First Stage.

Run no.	Duration, mins.	Yield of liquid products, c.c.	Sulphur in liquid product, c.c.	Sulphur in gas, g./hr.
52	60	22	0·91	—
53	120	48	0·87	0·50
54	180	113	2·28	—
55	245	180	3·60	0·49
56	335	250	—	—
57	395	340	3·92	—
58	425	380	5·56	0·17
59	520	510	7·00	—
60	525	515	—	—
61	690	691	—	0·10
62	840	861	7·88	—
63	910	941	7·54	—
64	920	951	—	—
65	1040	1051	8·36	0·13

TABLE XIII.

Desulphurization—Second Stage.

Run no.	Duration, mins.	Yield of liquid product, c.c.	Sulphur in liquid product, per cent.
66	60	35	6·61
67	150	95	7·96
68	270	221	6·30
69	315	277	12·8
70	395	372	—
71	505	—	10·1
72	520	384	11·9

Since sulphur dioxide was produced in the reactivation process, and as molybdenum sulphides are very stable, it is probable that some sulphur was sorbed by the catalyst carrier. The tests made were extremely severe, and the fact that the catalyst desulphurized to the extent of 60 per cent. after a 17-hour continuous run, without reactivation, and without any added hydrogen, indicates that it is very stable to sulphur, although from these results it is expected to be progressively poisoned over very long periods. It may be found, however, that when lower-percentage sulphur charges are treated no poisoning occurs, and that no sulphur is absorbed on the catalyst carrier. The second-stage experiment shows (Fig. 8) that the poisoning observed is in part reversible.

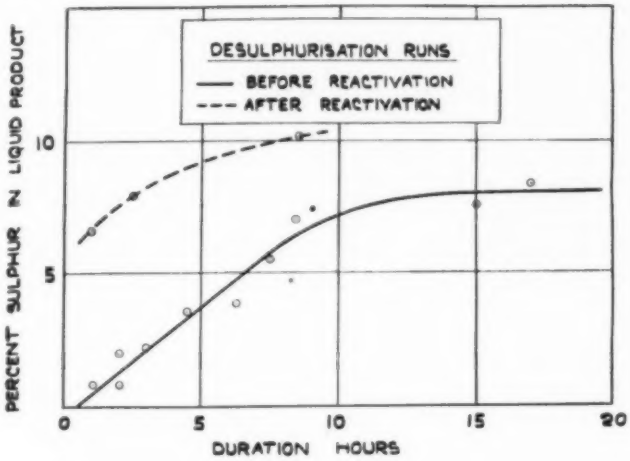

FIG. 8.

Thiophen Run.

A 1 per cent. sulphur (as thiophen) mixture was made in hexane and run over a new catalyst using the conditions of previous runs. The results are shown in Table XIV.

TABLE XIV.

Charge : 198 c.c. 1% sulphur (as thiophen) in hexane.
Product : 111 c.c. in three fractions : average percentage sulphur = 0·34 per cent.
28 litre of gas.

Run no.	Vol. liquid product, c.c.	Duration of run, hrs.	Percent. S. in liquid product.	Percent. benzene in liquid product.
78	31	—	0·10	60
79	30	1	0·53	60
80	50	1	0·38	51

Thiophen is thus much more difficult to remove under the conditions stated than is carbon disulphide, but the results indicate that the catalyst

is stable to sulphur in the charge when in the form of carbon disulphide or thiophen, and effectively desulphurizes in both cases.

Discussion.

Although the work reported here is not extensive and no light is thrown on the processes of poisoning and desulphurization, an important principle is indicated—that of complex catalysts where the complexity is due not to the catalyst but to the substrate itself. It is clear that with a molybdenum catalyst the processes of cyclization and desulphurization proceed together. It has been observed before [43] that molybdenum sulphide is an active catalyst for hydrogenation–dehydrogenation, as is molybdenum oxysulphide.[44]

When the spent catalyst from the desulphurization runs was analysed, however, the proportion of Mo to S was 0·81 atoms to 1 atom, hence it appears that the catalyst was a mixture of oxide and sulphide.

The greater resistance of thiophen to decomposition is probably due to the stability of the thiophen ring itself, but the fact that this compound is decomposed under cyclization conditions, together with the possibilities of conversion of near boiling non-aromatics to benzene and the stability of the latter under these conditions, serve to indicate the possible use of cyclization catalysis for the production of pure aromatics. In this connection it is worthy of note that some nitrogenous compounds are converted into ammonia and hydrocarbons during the cyclization reaction.[43]

Conclusion.

Table XV shows the most important experimental results which have not been tabulated above, and it can be seen that naphthalene formation was quite general in the cyclization reactions studied and usually formed about 1 per cent. of the product.

Table XV.

	Feed.	Catalyst.	Temp., °C.	Liquid catalyst space velocity, v./v./hr.	Loss, gas, carbon, etc., per cent.	Products : percentages on charge. (Liquid.)			
						Aromatics.	Unsats.	Paraffins.	Naphthalene.
1	Benzole	Copper chromite	500	0·3	—	Increase of 8%	Increase of 9%	—	1
2	n-Heptane	Mo_2O_3 on alumina	550	0·3	7	53 (toluene)	4	39	1
3	Technical heptene	Mo_2O_3 on alumina	550	0·20	38	14	19	29	—
4	Toluene	Mo_2O_3 on alumina	550	0·21	3	95 (toluene)	1–2	1–2	—
5	2 : 2 : 4-Trimethyl pentane	Mo_2O_3 on alumina	550	0·20	50	25	1	24	1
6	2 : 2 : 4-Trimethyl pentane	Cr_2O_3 on alumina	450	0·33	11	1–2	12–14	73	1
7	Hexane with 1 per cent. thiophen	Mo_2O_3 on alumina	550	—	—	50	—	—	—

Cr_2O_3 from chromic acid, on floridin as carrier, showed negligible activity, whereas when the sesquioxide was prepared from chromium nitrate, using the same carrier, the aromatics and unsaturateds in a hydrocarbon mixture were increased by 16 per cent.

Copper chromite and molybdenum sulphide on various carriers were active, but the introduction of activated alumina increased the activity of these and other catalysts considerably. Activated alumina alone was also active.

Various mixtures were passed over a molybdenum-alumina catalyst, and it was found that *n*-heptane is more easily aromatized than technical heptene. The reactions of other mixtures are discussed, and *o*-xylene was identified from the aromatization of 2 : 2 : 4-trimethyl pentane. At 550° C. 2 : 2 : 4-trimethyl pentane was converted into 25 per cent. aromatics, but this conversion was accompanied by extensive cracking.

Desulphurization and aromatization of benzole fractions were found to be technically inseparable processes. The activities of various catalysts for desulphurization were studied. Molybdenum sulphide showed greater activity than chromium sulphide, except when the former was prepared outside the catalyst tube.

In general, the cyclization of hydrocarbon mixtures results in a spreading of the distillation curve, formation of gas and carbon and an increase in aromatic and unsaturated hydrocarbons. At the same time hydrogenation reactions take place. The product from such a reaction will therefore depend on the conditions of the reaction and on the nature of the substrate. By the choice of suitable conditions, and by varying the composition of the substrate, it is possible to achieve several different reactions at the same time, using a single catalyst.

In a later paper the continuation of this work will be described, and the significance of some of the results may be seen in a different perspective.

The author wishes to express his appreciation for the interest and encouragement shown by the late Professor A. W. Nash and by Dr. T. G. Hunter of this Department.

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SPRING TENSION BALANCE FOR C.F.R. BOUNCING PIN.*

By P. Draper.†

Introduction.

An instrument was designed in 1939 by D. M. Clement, of the Shell Laboratory, London, for accurately determining the tension of the leaf-springs and plunger-spring on the C.F.R. adjustable-leaf-type bouncing-pin, the standard instructions for setting being inadequate, particularly when testing high-octane fuels.

After consideration by the Knock Rating of Aircraft Fuels Panel Sub-Committee of the Institute of Petroleum detail alterations were made, and the final apparatus proved so successful that it has been employed for some time in almost every C.F.R. installation in the United Kingdom and in many laboratories overseas.

Development.

The A.S.T.M. instructions for the setting of the old-type pin gave the limits of the free deflections, due to a permanent set of the lower and upper leaf-springs. These deflections were quoted in the A.S.T.M. procedure in sixty-fourths of an inch, and their limits were $\frac{3}{64}-\frac{4}{64}$ inch for the lower leaf-spring and $\frac{6}{64}-\frac{7}{64}$ inch for the upper leaf-spring. The plunger-spring tension must be within 1·0–1·25 lb.

The above deflections were measured with an initial contact gap of 0·005 inch and the pin then removed.

For simplicity, these deflections are now designated in thousandths of an inch with the gap just closed when the pin is in position, thus :—

The limits for the lower leaf are . .	0·042–0·057 inch
The limits for the upper leaf are . .	0·099–0·114 inch

It has been experienced that the deflection-load characteristics of all springs supplied are not similar. Springs in service become buckled and also lose their elasticity; new springs have not precisely similar dimensions and elasticity. Consequently there has been no definite knowledge or control of the forces of the springs acting on the pin. This instrument can determine true spring tensions in grams while the springs are in position.

The deflection-load characteristics of a number of springs gave the

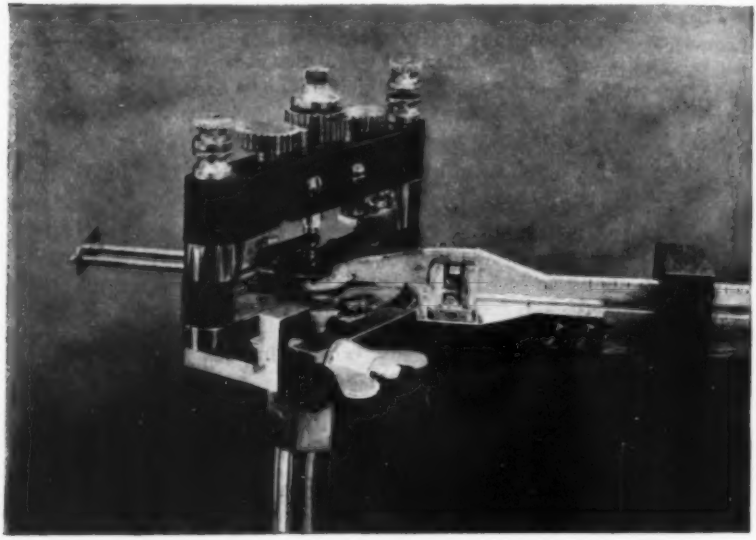
* Paper received 18th July, 1942.
† Asiatic Petroleum Co., Ltd.

following average figures for the forces in grams when the springs were deflected to the extent given by the A.S.T.M. upper and lower limits.

		Force in grams.
Lower leaf-spring deflection . . .	0·042 inch	180
	0·057 „	245
Upper leaf-spring deflection . . .	0·099 „	380
	0·114 „	440
Plunger pressure	1 lb.	454
	1·25 lb.	568

The Instrument.

The instrument is simply a beam balance 9 inches in length, pivoted on a knife-edge (see drawings and photograph). The assembly is clamped to the flange of the bouncing-pin body, and made rigid by the tightening of



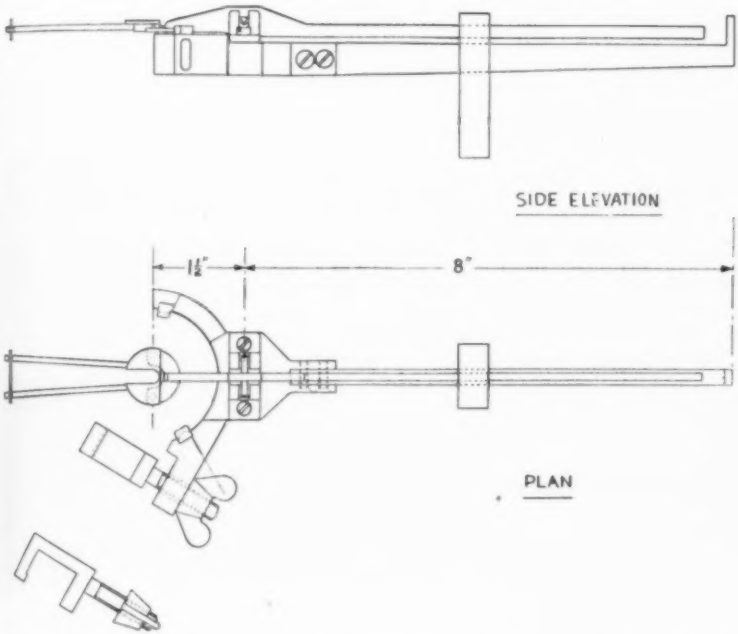
a thumb-screw. No part of the pin need be dismantled for this purpose. (The bouncing-pin assembly may remain in the engine or it may be held vertically in a vice.)

The inner end of the beam is forked, and bears at two points upon the underside of a thin clamp, which is attached to the tip of the pin protruding from the pin body. An imaginary line through the two bearing points passes through the vertical axis of the pin, thus a true value of the forces required to deflect the springs may be determined. A jockey weight on the outer arm balances the combined force of the spring to be tested and the weight of the pin and collar. The beam is calibrated from 150 to 570

grams at intervals of 10. A reading may be made to half a division, which is the limit of accuracy. (The average weight of the pin and the small clamp have been allowed for in the calibration of the beam.)

Application.

It should be appreciated that the lower leaf-spring provides a downward force restraining the movement of the bouncing-pin, and thus causing the contacts to close only during detonating conditions. The upward force of the upper leaf-spring and the downward force of the plunger provide a nett " buffer " force for the bouncing-pin and lower leaf-spring to bounce against. It is this nett " buffer " force which determines the duration of electrical contact of the contact points, and therefore the sensitivity of the circuit.



After the bouncing-pin assembly has been dismantled for cleaning and re-assembled, the spring-tension should be checked in the following sequence :—

1. *Plunger Tension.*

Swing aside the two leaf-springs by loosening their mounting screws at the ends of the lower cross-bar.

Raise the pin until it touches the plunger, and attach the pin-clamp

to the pin so that there is $\frac{3}{16}$ inch between its under face and the bouncing-pin body.

Mount the beam and adjust the plunger tension to 455 and 570 grams, marking the positions of the adjusting screw for future reference.

Leave the plunger set at 530 grams.

(The figure on the beam-scale flush with the inner surface of the jockey weight will give the force in grams.)

2. *Lower Leaf-spring Tension.*

Reassemble the two leaf-springs, seeing that they are correctly aligned, and set the contact gap to approximately 0·001 inch.

Attach the pin-clamp to the pin so that there is $\frac{3}{16}$ inch between its under face and the bouncing-pin body.

Mount the beam and adjust the spring-tension screw so that the contact gap just closes at 180 and 245 grams marking the adjusting screw for future reference.

Leave this spring set at 180 grams.

3. *Upper Leaf-spring Tension.*

The upward tension of this spring can be determined only by measuring the combined force of all the springs, and thence by calculation. This is obtained by continuing to load the beam until the plunger is about to be moved.

The upper spring tension-screw should be adjusted to give beam loadings of 270 and 330 grams marking the positions of the adjusting screw for future reference.

The setting should be left at 310 grams.

(The method of arriving at the above figures is as follows :—

The total downward tension of the three springs is equal to the sum of the tensions of the plunger and the lower leaf-spring, less the upward tension of the upper leaf-spring.

$$\begin{aligned}\text{Total downward tension} &= 530 + 180 \begin{matrix} - 440 \\ - 380 \end{matrix} \text{ grams.} \\ &= 710 \begin{matrix} - 440 \\ - 380 \end{matrix} \text{ grams.} \\ &= 270 \text{ and } 330 \text{ grams.}\end{aligned}$$

From experience it has been found that for maximum knockmeter sensitivity the nett balancing force of the plunger and upper leaf-spring should be about 130 grams. Therefore 530 and 400 grams have been chosen for the initial setting of these springs. The total downward tension is thus $710 - 400 = 310$ grams.)

4. Remove the spring-tension apparatus and set the contact gap to 0·003 inch (its limits being 0·003–0·005 inch.)

The bouncing-pin is then set for operation, and a minimum of alteration should be made within the limiting marks made on the adjusting screws. No alteration is permissible outside these limits.

Subsequent Setting.

A 55–60 knockmeter reading should be obtainable under standard conditions of operation by *very slight* adjustment of the contact gap within the limits specified above.

For testing high-octane fuels it may be necessary to increase the downward tension of the lower leaf-spring to a maximum of 245 grams. See Institute of Petroleum Standard Methods 1942. (For testing by the 17° Motor Method it may be necessary to increase the tension to 300 grams. See *J. Inst. Pet.*, May 1941, Vol. 27, p. 191).

It should not be necessary to alter the settings of the plunger or upper leaf-spring, but the sensitivity of the knockmeter depends on these relative settings. (Provided that the lower leaf-spring is exerting sufficient downward force to prevent the recording of " combustion pressures ".)

Notes.

The following approximate figures may be useful :—

One notch on the plunger-screw is equivalent to approximately 15 grams tension on the plunger.

One notch on the lower spring-screw is equivalent to approximately 10 grams tension on the pin.

One notch on the upper spring-screw is equivalent to approximately 10 grams tension.

Care should be taken that the reading of the number of notches of turn of the upper spring-screw is not a false one on account of the backlash.

OBITUARY.

JAMES ROMANES.

In the sudden and premature death of James Romanes at the early age of 56, Great Britain loses one of its most talented and respected geologists and authorities on oilfield geology. Following his education at the Edinburgh Academy, he proceeded to Christ's College, Cambridge, where his inherited inclinations and outstanding abilities were concentrated on geology, and he there obtained his B.A. (Natural Science Tripos, 1st Class) in 1908, and Natural Science Tripos, Part 2, 1st Class Geology, in 1909. He was Harkness University Scholar in 1911 and became an M.A. in 1912. For a time he remained at the University as lecturer and coach in geology, whilst engaged on research work, thereby becoming acquainted with many students who sought his advice and guidance when building a career and later acquired distinction. One of his earliest associations with oil was on an expedition that had for its object the determination of oil prospects in the Eastern Andean foothills of Bolivia, a task which involved two years' absence in remote and inhospitable country.

The European War of 1914–18 caused a break in his professional activities, for he at once joined up, and obtained a commission in a Border regiment that was eventually drafted to Gallipoli. At Suvla he was gravely wounded when leading his company in an attack on Turkish positions, and was reported killed; indeed, his obituary notice appeared in *The Times*, and his family went into mourning. On recovering from his wounds he accepted a post with the Royal Flying Corps, where his scientific accomplishments were quickly recognized and applied in investigations of a confidential nature. When peace was proclaimed and he secured his release from the Army with the rank of Colonel, he renewed his connection with the petroleum industry, and became a partner in the firm of A. Beeby Thompson and Partners, where his great organizing, scientific and commercial abilities found full scope in directing and supervising topographical and geological surveys connected with petroleum and water projects. Romanes was closely identified with oil exploration in Trinidad, Barbados, Germany, Portugal, Irak and Syria, and amongst his various foreign excursions was one to Iceland and another to Teneriffe. He contributed articles to the *Encyclopaedia Britannica*, and sought by many Press articles to attract public interest in the London Water Supply by proposals to recharge the depleted London Basin with water from the Thames at times of flood.

Romanes had served on the Councils of the Geological Society and Institute of Petroleum, and he was very actively associated with the Mining Club. He was a gifted and lucid speaker and writer, and in debate he was blunt and forceful, but always willing to concede a point which merited respect. His great charm of manner and fund of dry humour attracted many friends, and at West Byfleet his ready willingness to help in any social or patriotic movement led him to take a keen interest in golf and to initiate the Home Guard movement in his district.

A. B. T.